CHEMICAL SOIL PHYSICS PHENOMENA
FOR CHEMICAL SENSING OF BURIED UXO

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Abstract

Technology development efforts are under way to apply chemical sensors to discriminate inert ordnance and clutter from live munitions that remain a threat to reutilization of military ranges. However, the chemical signature is affected by multiple environmental phenomena that can enhance or reduce its presence and transport behavior, and can affect the distribution of the chemical signature in the environment. For example, the chemical can be present in the vapor, aqueous, and solid phases. The distribution of the chemical among these phases, including the spatial distribution, is key in designing appropriate detectors, e.g., gas, aqueous or solid phase sampling instruments. A fundamental understanding of the environmental conditions that affect the chemical signature is needed to describe the favorable and unfavorable conditions of a chemical detector based survey to minimize the consequences of a false negative. UXO source emission measurements are being made to estimate the chemical flux from a limited set of ordnance items. Phase partitioning analysis has been completed to show what the expected concentrations of chemical analytes would be from total concentrations measured in the soil. The soil moisture content in the dry region has been shown to be critical in the attenuation of soil gas concentrations by increased sorption to soil particles. Numerical simulation tools have been adapted to include surface boundary conditions such as solar radiation, surface boundary layer (which is a function of wind speed), precipitation and evaporation, and plant cover/root density to allow transport modeling and evaluate long term processes. Results of this work will provide performance targets for sensor developers and support operational decisions regarding field deployments.

Fundamental Properties of Explosives in the Soil Environment

Much has been written on the fundamental chemistry and soil chemodynamics of explosives in the soil environment. Our initial effort reported that the principal explosive constituents, TNT and 2,4-DNT, are principally found in sorbed to the soil solid phase and in the soil water, with only a very minor mass fraction in the soil air (Phelan and Webb, 1997). This is driven principally by the very low vapor densities of these materials and moderate soil-water partitioning coefficients. Considering the UXO discrimination problem, soil adjacent to buried UXO items will likely be a significant reservoir for the explosive constituents. One of the challenges for field execution of chemical sensing is that vapor sniffing technology is significantly less difficult than soil sampling and analysis because detector technology typically uses vapor or liquid phase sample introduction.

Transport of the explosive chemical signature far away will be retarded, retaining a localized feature suitable for use in discriminating live HE containing UXO from target practice rounds. Transport of the

chemical signature from the UXO item to the ground surface might be one phenomena that might be exploited to locate buried UXO items. Further examination of the transport processes is complicated by the wetting and drying processes from precipitation events. The following section examines the effect of increased vapor sorption on dry soils.

Vapor Solid Phase Partitioning Analysis

The environmental fate and transport of organic chemicals including volatilization and leaching losses has been used to explore the distribution of agricultural pesticides in soils (Mayer et al. 1974, Farmer et al. 1980, and Jury et al. 1980). These models were primarily intended to simulate specific circumstances. However, Jury et al. (1983, 1984a, 1984b, 1984c) developed and validated a general screening model (Behavior Assessment Model, BAM) that included volatilization, leaching, and degradation to explore the major loss pathways of agricultural pesticides as a function of specific environmental conditions. The Behavior Assessment Model was adapted for evaluation of chemicals in buried soils and has been termed the Buried Chemical Model (BCM)(Jury et al., 1990). This model can be used to assess the behavior of different explosive signature chemicals under particular environmental conditions to evaluate the potential of chemical signature discrimination of UXO.

The formulations of the BAM and BCM models begin by defining phase partitioning phenomena. These are valuable in that they can express the total concentration of a chemical in the gas, aqueous and sorbed phases. The total concentration is expressed as

$$C_T = r_b C_S + q C_L + a C_G \qquad [1]$$

where C_S is the concentration sorbed to the soil, C_L is the solute concentration in the aqueous phase, and C_G is the gas phase concentration. In addition, Jury (1983) shows how equation [1] can be rewritten in terms of one of the variables alone

$$C_T = R_S C_S = R_L C_L = R_G C_G \qquad [2]$$

where

$$R_S = r_b + \frac{q}{K_d} + a \frac{K_H}{K_d} \qquad [3]$$

$$R_L = r_b K_d + q + a K_H, \text{ and} \qquad [4]$$

$$R_G = r_b \frac{K_d}{K_H} + \frac{q}{K_H} + a \qquad [5]$$

are the solid, liquid and gas phase partition coefficients, respectively.

In their evaluation of vapor phase transport in soils, Ong et al., 1992, added vapor-solid sorption such that equations [1] and [2] become

$$C_T = q C_L + a C_G + C_L K_d r_b + C_G K_{SG} r_b \qquad [6]$$

and

$$C_T = R_S C_S = R_L C_L = R_G C_G = R_{SG} C_{SG} \qquad [7]$$

where

$$R_L = r_b K_d + q + a K_H + r_b K_H K_{SG} \qquad [8]$$

$$R_G = r_b \frac{K_d}{K_H} + \frac{q}{K_H} + a + r_b K_{SG} \qquad [9]$$

$$R_{SL} = r_b + \frac{q}{K_d} + a \frac{K_H}{K_d} + \frac{r_b K_H K_{SG}}{K_d} \text{, and} \qquad [10]$$

$$R_{SG} = \frac{r_b K_d}{K_H K_{SG}} + \frac{q}{K_H K_{SG}} + \frac{a}{K_{SG}} + r_b \qquad [11]$$

are the liquid, gas and solid-liquid and solid-gas phase partition coefficients, respectively.

This formulation introduces a new term, K_{SG} that is a function of the overall vapor partition coefficient (K_d), which is highly dependent on the soil moisture content. K_{SG} is defined as (Ong et al., 1992)

$$K_{SG} = K'_d(w) - \frac{K_d}{K_H} + \frac{w}{100 K_H g r_w} \qquad [12]$$

Below four monomolecular layers of water coverage on soils, K_d is an exponential function described by

$$A = \log(K'_d) \qquad [13]$$

$$A = (A_0 - b(w)) e^{-aw} + b(w) \qquad [14]$$

$$a = \frac{-\ln\left[\dfrac{A_4 - b}{A_0 - b}\right]}{w_4} \qquad [15]$$

$$b(w) = \log\left(\frac{K_d}{K_H} + \frac{w}{K_H g r_w}\right) \qquad [16]$$

Above four monomolecular layers of water coverage on soil, K_d is a function of K_H and is described by

$$A = \log\left(\frac{K_d}{K_H} + \frac{w}{K_H g r_w}\right) \qquad [17]$$

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Ong et al, 1990, characterize the vapor-solid partitioning in this region as being controlled by Henry's Law Constant (HLC). This is because the vapor must first partition into the soil water prior to partitioning onto the soil particle. The moisture content at four monomolecular layers of soil water is a function of the soil specific surface area and is described by

$$w_4 = 4\left(\frac{S_A MW_w}{MA_w A_n}\right)$$

[18]

The specific surface area (S_A) of soils range from 10 m^2/g for sand to 100's m^2/g for some types of clay. Figure 1 shows the correlation of soil specific surface area to the moisture content at four monomolecular layers of water. The proportion of clay in soils strongly influences the soil specific surface area. This is due to the small size of the clay soil particles.
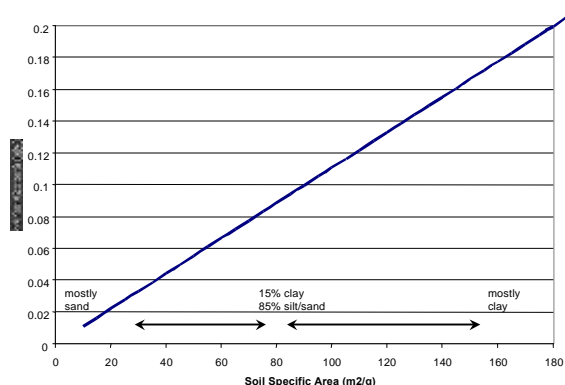

Figure 1. Soil Water Content at 4 Monomolecular Layers as a Function of Soil Specific Area

In their evaluation of toluene and trichloroethene, K_d increased about 10^4 from the point of four monomolecular layers to oven dry soil moisture contents. The impact of the vapor solid partitioning is significant at moderately low soil moisture contents. Figure 2 shows how the relative soil gas concentration can decline rapidly as the soil moisture content declines. Note that the soil moisture contents at four monomolecular layers are at levels that are not unusually low, and are typically observed in soils after precipitation and drainage events have occurred. With an extended absence of precipitation, the surface soil moisture approaches the extremely dry region. It is a potential that this dry layer could act as a barrier to vapor emission from soils and be a preconcentrator of analyte signal. Whether this process is fully reversible with the addition of water is unknown, and may represent an opportunity for enhancement of the chemical signature.
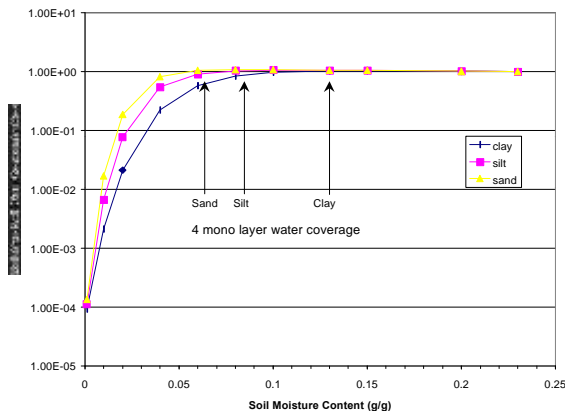

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Figure 2. Relative Soil Gas Concentrations Impacted by Low Soil Moisture Content

In order to understand this phenomenon more, a Monte Carlo simulation approach was employed. This method specifies a statistical distribution function for various input parameters, then randomly selects particular values for each input variable within the specified statitical distribution, and tracks the output of one or more variables. The following input assumptions and distributions were defined for the soil bulk density, soil particle density, soil moisture content, soil water partition coefficient, soil specific surface area and soil vapor partition coefficient at oven dry conditions (A_0). Other parameters that were fixed included soil temperature (22 °C), which defines the Henry's Law Constant, the soil specific surface area (80 m^2/g) which defines the soil moisture content at four monomolecular layers (0.089 g/g) and the total soil concentration (C_T = 1000 ug/kg). The chemical chosen for this simulation was 2,4-DNT, as it may likely be one of the best signature compounds for chemical detection.

Two forecast evaluations were performed. The first was for soil moisture contents that were above the four monomolecular layers of soil water (0.13 to 0.30 cm^3/cm^3) such that the vapor solid partition coefficient was in the region controlled by the HLC. The volumetric moisture content of 0.13 cm^3/cm^3 is equivalent to a gravimetric soil mositure content of 0.089 g/g at a soil bulk density of 1.5 g/cm^3, which is the soil moisture content at four monomolecular layers for a soil with a specific area of 80 m^2/g. The output variable is the soil gas concentration. The second forecast evaluation was performed in the dry region, below four monomolecular layers of soil water (0.01 to 0.13 cm^3/cm^3), where the soil vapor partioning is highly non-linear.

Figure 3 shows the forecast of soil gas concentrations indicating a range of values from 100 to 750 parts per trillion with an apparent normal or log normal distribution of values.
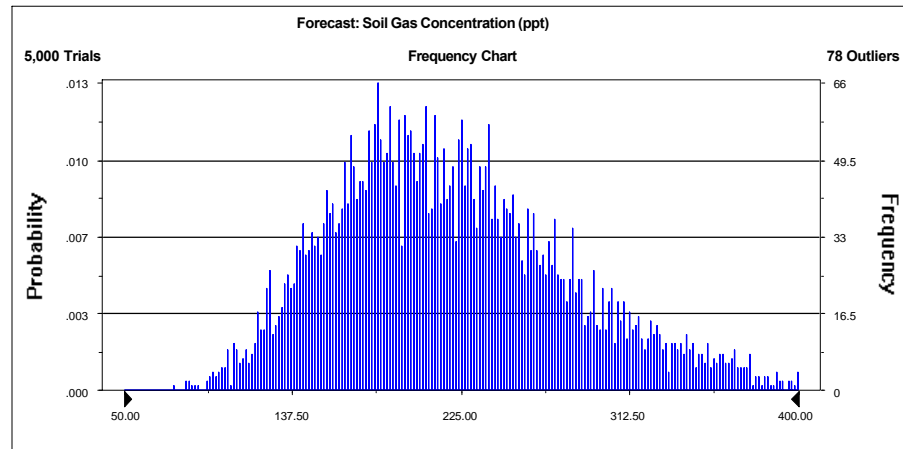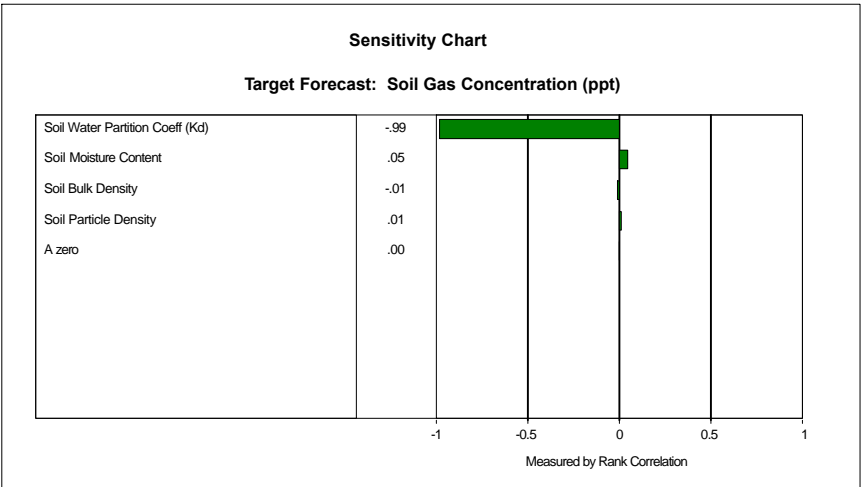

Figure 3. Soil Gas Concentration – Wet

Figure 4 shows a sensitivity analysis of the input parameters. The strongest parameter is the soil water partition coefficient, which is clear from a closer examination of equation [9]. The shape of the histogram in Figure 3 is consistent with that for the soil water partition coefficient, which is also supported by the strength of the association as shown in the sensitivity analysis (Figure 6).

The next simulation was performed by altering only the input values for the soil moisture content. In this case, the soil moisture range is set to be below four monomolecular layers of water.

Figure 5 shows that most of the forecast values for the soil gas concentration are well below those for the

Sensitivity Chart

Target Forecast: Soil Gas Concentration (ppt)

Soil Water Partition Coeff (Kd)	-.99
Soil Moisture Content	.05
Soil Bulk Density	-.01
Soil Particle Density	.01
A zero	.00

Measured by Rank Correlation

higher moisture content simulation. In addition, the sensitivity analysis (Figure 6) shows that the principal parameter is now the moisture content, as $K_d(w)$ becomes dominant (equations [9] and [12]).
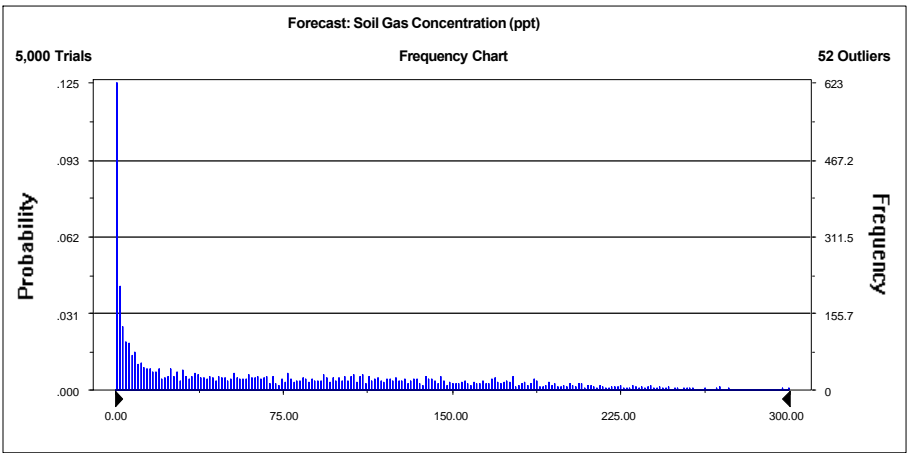
Figure 4. Sensitivity Analysis – Wet

Forecast: Soil Gas Concentration (ppt)

5,000 Trials   **Frequency Chart**   **52 Outliers**

Figure 5. Soil Gas Concentration - Dry

Sensitivity Chart

Target Forecast: Soil Gas Concentration (ppt)

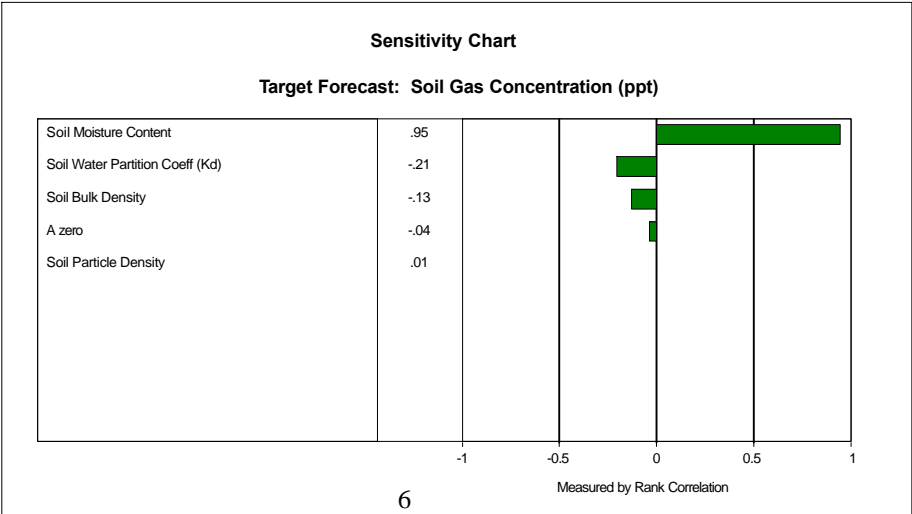|	
Soil Moisture Content	.95
Soil Water Partition Coeff (Kd)	-.21
Soil Bulk Density	-.13
A zero	-.04
Soil Particle Density	.01

Measured by Rank Correlation

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Figure 6. Sensitivity Analysis – Dry

This analysis shows that under very dry soil conditions, one that might be found after an extended time with little or no precipitation, the soil vapor concentrations will be dramatically depressed. However, it is uncertain whether the mass of explosive signature sorbed to the soil can be released upon wetting. Some laboratory evidence indicates this occurs, and might be used in the field by watering areas prior to performing a vapor sensing survey.

Screening Model Analysis

A one-dimensional model sensitivity analysis was used to examine the impact of changes to a single parameter for a given environmental scenario. The output that was evaluated was the surface vapor flux. The model that was used was the Buried Chemical Model from Jury et al., 1990. Details of this simulation model can be found in Phelan and Webb, 1997, 1998a, and 1998b. Table one shows the parameters evaluated and a summary of the impact.

Table 1. Screening Model Sensitivity Analysis Summary

Parameter	Impact on steady state surface flux
Soil Bulk Density	Direct inversely proportional
Henry's Law Constant	Directly proportional
Soil-Water Partition Coefficient	Direct inversely proportional
Source Flux	Insignificant compared to initial surface concentration
Initial Surface Concentration	Directly proportional
Burial Depth	Increases lag time (very sensitive)
Water Flux (Precipitation or Evaporation)	Evaporation enhances, precipitation depresses
Biochemical Half-life	Insensitive if > 1 year, very sensitive if < 60 days

A 2-dimensional analysis was performed which showed that the surface vapor flux was greatest directly above a source with a small halo up to twice the length of the buried source. However, the flux drops off exponentially with lateral distance.

Numerical Simulation Tools

A more detailed mechanistic numerical model is being developed. This model is being based on TOUGH2 (Pruess, 1991) with modifications pertinent to the UXO/landmine application and is called T2TNT. The first round of modifications to TOUGH2 has been completed including:

1. Addition of TNT, DNT, and DNB vapor components – UXO/landmines typically emit TNT, DNT, and DNB vapors. The behavior of each of these chemicals is different (vapor pressure, vapor/liquid, liquid/solid, and vapor/solid partitioning), so each component is modeled separately. Additional components could be added if necessary.
2. Dusty Gas Model for gas diffusion – Gas diffusion can be a dominant transport mode for explosive vapors in the subsurface, especially for low moisture content conditions. In order to mechanistically model gas diffusion in a porous medium, the Dusty Gas Model (Webb, 1998) has been implemented.

3. Liquid diffusion of dissolved explosive gases – Liquid diffusion can be a dominant transport mode for explosive vapors in the subsurface, especially for moderate and high moisture content conditions. Liquid diffusion was not present in the original version of TOUGH2. Liquid diffusion using Fick's Law has been included because of the significant chemical concentration in the liquid phase.
4. Partition coefficient as a function of saturation – The solid partition coefficient may be a strong function of saturation, especially at low moisture content where the partition coefficient may increase dramatically (Petersen, et al. 1995). The capability of including a saturation-dependent partition coefficient has been included.
5. Biodegradation – A simple half-life approach has been implemented to model biodegradation of the explosive vapors.
6. Surface Boundary Conditions – Due to the shallow burial depth of many UXO/landmines, the fluid conditions surrounding the UXO/landmine are strongly influenced by the surface conditions. The parameters necessary to adequately model the surface boundary conditions are numerous, including solar and long-wave radiation, the surface boundary layer which is a function of wind speed and other parameters, precipitation and evaporation at the surface, plants and their root systems, and the diurnal and seasonal variation of these parameters. The models used for these boundary conditions are discussed in more detail below.

The surface boundary conditions discussed above are complex in their own right. Numerous models have been developed to analyze the soil-air-plant system. In order to expedite the inclusion of the important surface conditions into T2TNT, a number of existing models have been evaluated. As a result, the SiSPAT model developed by Braud et al. (1995, 1996) has been selected for inclusion into T2TNT with the kind permission of M. Vauchlin of LTHE in Grenoble, France. Subroutines from SiSPAT have been included directly into T2TNT as necessary.

SiSPAT has been applied to a number of field studies as documented by Braud et al. (1995, 1995), and Boulet et al. (1997), and more are in progress. Therefore, SiSPAT should provide a well-documented and tested approach for modeling the soil-plant-atmosphere interface in the T2TNT code.

At the present time, the surface boundary conditions for a bare soil have been implemented, including the surface boundary layer, solar and long-wave radiation, precipitation, and other conditions including the diurnal and seasonal variation of the parameters. Incorporation of the plant portion of the SiSPAT model into T2TNT is expected in 1999.

As part of the verification process for T2TNT, comparison to results of the one-dimensional screening model presented by Phelan and Webb (1997) have been performed. The conditions are for a low desert environment with moderate moisture content; the parameters are the same as found in Phelan and Webb (1997). The precipitation/evaporation cycles have not been included in this simulation in order to provide comparison with the buried chemical analytical solution of Jury et al. (1990).

Note that some of the assumptions made in the analytical model can only be approximated in the numerical code, such as uniform moisture content. In addition, there are differences in the gas diffusion model, which could lead to slightly different answers. However, in general, the analytical and numerical problems are essentially equivalent.

Figure 7 compares the TNT flux at the surface from the analytical solution and from T2TNT. The predicted surface flux values are higher than the analytical solution, especially at smaller times. The difference is due to numerical diffusion of the numerical method and is expected. At longer times, the agreement between the analytical and T2TNT solutions is good.
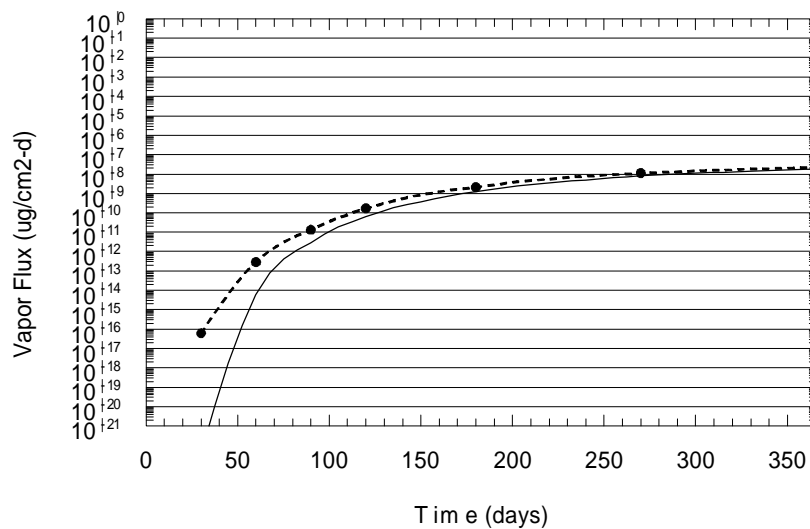
Figure 7. Comparison of TNT surface flux from Analytical and Numerical Models

Figure 8 shows the subsurface distribution of TNT after 1 year for the Jury et al. (1990) model and from T2TNT. The agreement in the concentration distribution is excellent at all locations. Overall, the solution from T2TNT agrees well with the analytical solution of Jury et al. (1990) except for some surface flux differences at early times due to numerical diffusion.

Additional verification and sensitivity studies will be performed with the newly-developed model, including the effect of the boundary layer on the results, drying simulations including non-uniform
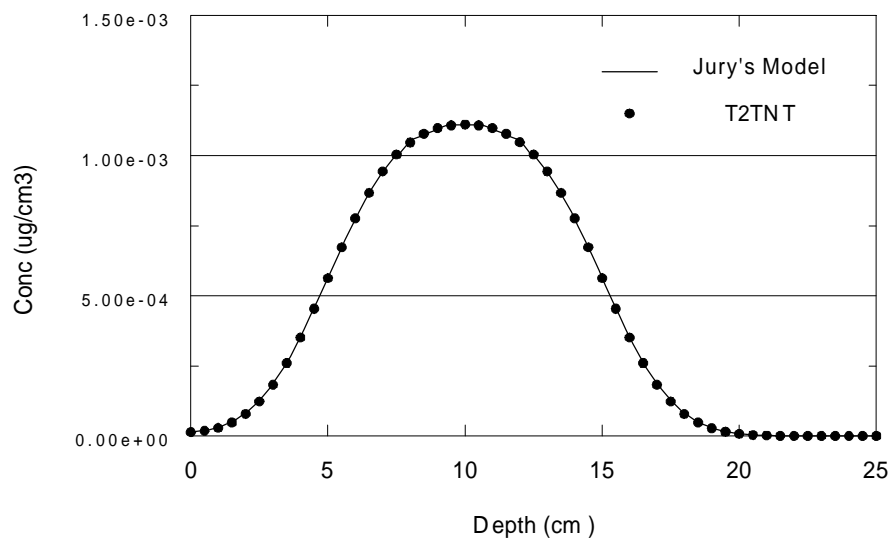

Figure 10. Comparison of Depth Profile from Analytical and Numerical Models

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moisture content, diurnal and seasonal variations, and multidimensional effects to determine the degree of lateral spreading including the "footprint" of a landmine.

Acknowledgments

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